

$10^{-7} \text{ S m}^2 \text{ J}^{-1}$  for  $\text{H}_2\text{P}$  and  $\text{ZnP}$  respectively at room temperature. The presence of the central zinc atom therefore seems to increase the conductive properties of the solid slightly.

In Fig. 2,  $(\Delta\sigma/D)_0$  is plotted as a function of temperature. For  $\text{H}_2\text{P}$ , a single, sharp decrease occurs at the transition from the solid to the isotropic liquid. No conductivity could be detected in the isotropic phase. For  $\text{ZnP}$ , the conductivity decreases abruptly, but does not disappear completely, at the solid to liquid-crystal transition temperature. The conductivity in the mesophase is a factor of  $\sim 3$  less than in the solid with  $(\Delta\sigma/D)_0 = 0.5 \times 10^{-7} \text{ S m}^2 \text{ J}^{-1}$ . This increases slightly with further increase in temperature in the mesophase and then suddenly drops to zero at the clearing point of  $\text{ZnP}$ .

We conclude that the long-range columnar order of porphyrin moieties in the solid and liquid-crystalline phases is essential for the conductive properties observed. In the isotropic liquid phase, any molecular organization that might occur must be of such a limited temporal or geometrical extent that it cannot support charge conduction. The results provide definitive evidence, therefore, for the general supposition that electrons and/or holes can move rapidly along the axis of column-stacked  $\pi$ -systems<sup>5,6</sup>. The decrease in conductivity on going from the crystalline solid to the mesophase is attributed to a lower charge mobility. This is probably due to an increase in positional disorder of the porphyrin moieties<sup>7</sup> on melting of the hydrocarbon mantle.

We have found a similar decrease in the radiation-induced conductivity at the solid to mesophase transition of octa-alkoxy-substituted phthalocyanines. An isotropic liquid phase of these compounds is not, however, attainable within the temperature range of our equipment. They could not therefore be used to carry out the conclusive experiment of completely melting the material to see if long-range order was essential for conduction. The experiments on octa-*n*-alkoxy substituted phthalocyanines have, however, shown that the lifetime of the conductivity transient increases exponentially with the length of the alkyl tails<sup>8</sup>. This is taken to be strong evidence that the mobile charge carriers responsible are restricted to rapid diffusional motion along the phthalocyanine axis of a stack, with eventual charge recombination requiring stack-to-stack electron tunnelling through the hydrocarbon mantle.

The absolute value of  $(\Delta\sigma/D)_0$  is related to the mobilities,  $\mu$ , of the charge carriers,  $\sum \mu = (\mu(-) + \mu(+))$ , and the average energy required to produce one charge-carrier pair,  $E_p$  (in eV), by<sup>3,4</sup>

$$(\Delta\sigma/D)_0 = \sum \mu / E_p \quad (1)$$

For organic compounds, the total initial yield of electron-hole pairs corresponds to a value of  $E_p$  of  $\sim 25$  eV for high-energy radiation<sup>9-11</sup>. Only a fraction of the initial electrons and holes will escape rapid (subnanosecond) geminate recombination<sup>8,9</sup> and diffuse to separate columns, thus being observed in the present experiments. Using a value of  $E_p = 25$  eV together with the experimentally determined value of  $(\Delta\sigma/D)_0$  will therefore yield a lower limit to the charge-carrier mobilities. For the solid phase of  $\text{ZnP}$  at room temperature, assuming electrons and holes to have almost equal mobilities<sup>12</sup>, this gives  $\mu > 2.6 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  and for the mesophase, it gives  $\mu > 0.6 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

This order of magnitude of the mobility indicates small polaron motion<sup>13</sup> corresponding to the hopping of a more or less localized charge between neighbouring sites with an average jump time between sites of  $\tau_j$ . The mobility measured in the present, randomly orientated columnar materials is related to  $\tau_j$  by

$$\tau_j = ed_j^2 / 6k_B T \mu \quad (2)$$

where  $d_j$  is the distance moved along the columnar axis per jump (4.9 Å for the present systems). The minimum values of the carrier mobilities given above correspond therefore to

maximum jump times of 0.6 and 2 ps for solid  $\text{ZnP}$  at room temperature and the mesophase at 100 °C, respectively.

Our results confirm that the transport of charge can occur very rapidly within an organized self-assembly of porphyrin moieties even in a relatively flexible, liquid crystalline phase. Such peripherally hydrocarbon substituted compounds may therefore be considered to provide model systems which crudely mimic the channelling of energy and charge found in the highly varied antenna chlorophyll arrays of photosynthetic membranes.  $\square$

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1. Gregg, B. A., Fox, M. A. & Bard, A. J. *J. Am. chem. Soc.* **111**, 3024-3029 (1989).
2. Weber, P., Guillon, D. & Skoulios, A. *Liq. Cryst.* **9**, 369-382 (1991).
3. Warman, J. M. & de Haas, M. P. in *Pulse Radiolysis*, Ch. 6. (ed. Tabata, Y.) 101-133 (CRC, Boca Raton, 1991).
4. Warman, J. M. & de Haas, M. P. *Radiat. Phys. Chem.* **34**, 581-586 (1989).
5. Eley, D. D. *Molec. Cryst. Liq. Cryst.* **171**, 1-21 (1989).
6. Simon, J. & André, J.-J. *Molecular Semiconductors* (Springer, Berlin, 1985).
7. Pietro, W. J., Marks, T. J. & Rainer, M. A. *J. Am. chem. Soc.* **107**, 5387-5391 (1985).
8. Warman, J. M., de Haas, M. P., van der Pol, J. F. & Drenth, W. *Chem. Phys. Lett.* **164**, 581-586 (1989).
9. Warman, J. M. in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis* (eds Bazendie, J. H. & Busi, F.) 433-533 (Reidel, Dordrecht, 1982).
10. Schmidt, W. F. & Allen, A. O. *J. Phys. Chem.* **72**, 3730-3736 (1968).
11. Shinsaka, K. & Freeman, G. R. *Can. J. Chem.* **52**, 3495-3506 (1974).
12. Cox, C. A. & Knight, P. C. *J. Phys. C* **7**, 146-156 (1974).
13. Mott, N. F. *Conduction in Non-Crystalline Materials*, Ch. 6 (Clarendon, Oxford, 1987).

ACKNOWLEDGEMENTS. We thank M. Northolt and S. J. Picken (AKZO Research Laboratories, Arnhem) for X-ray diffraction analysis of the  $\text{ZnP}$  compound and for helpful discussions. The synthetic work was sponsored by the Texas Advanced Technology Program.

## A low-cost, high-efficiency solar cell based on dye-sensitized colloidal $\text{TiO}_2$ films

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THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods<sup>1</sup>. Here we describe a photovoltaic cell, created from low-to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10- $\mu\text{m}$ -thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1-7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12  $\text{mA cm}^{-2}$ ) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

Solar energy conversion by photoelectrochemical cells has been intensively investigated<sup>2-11</sup>. Dye-sensitized cells differ from the conventional semiconductor devices in that they separate the function of light absorption from charge carrier transport. In the case of *n*-type materials, such as  $\text{TiO}_2$ , current is generated when a photon absorbed by a dye molecule gives rise to electron injection into the conduction band of the semiconductor, Fig. 1. To complete the circuit, the dye must be regenerated by

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electron transfer from a redox species in solution which is then reduced at the counter electrode. The monochromatic current yield

$$\eta_i(\lambda) = \text{LHE}(\lambda) \times \phi_{\text{inj}} \times \eta_c \quad (1)$$

where LHE (light harvesting efficiency) is the fraction of the incident photons that are absorbed by the dye,  $\phi_{\text{inj}}$  is the quantum yield for charge injection and  $\eta_c$  is the efficiency of collecting the injected charge at the back contact, expresses the ratio of measured electric current to the incident photon flux at a given wavelength. The photovoltage  $\Delta V$  in Fig. 1, generated by the cell, corresponds to the difference between the Fermi level in the semiconductor under illumination and the Nernst potential of the redox couple in the electrolyte.

Although attempts to use dye-sensitized photoelectrochemical cells in energy conversion have been made before, the efficiency of such devices has been extremely low and practical applications have seemed remote. One problem is that of poor light harvesting. On a smooth surface, a monomolecular layer of sensitizer absorbs less than 1% of incident monochromatic light. Attempts to harvest more light by using multilayers of dye have in general been unsuccessful. The remaining option is to increase the roughness of the semiconductor surface so that a larger number of dye molecules can be adsorbed directly to the surface and can simultaneously be in direct contact with the redox electrolyte. Matsumura *et al.*<sup>12</sup> and Alonso *et al.*<sup>13</sup> have used sintered ZnO electrodes to increase the efficiency of sensitization by rose bengal and related dyes. Willig, Parkinson and colleagues<sup>14</sup> have reported high quantum yields for the dye sensitization of  $\text{SnS}_2$ . But the conversion yields from solar light to electricity remained well below 1% for these systems. In addition, the instability of the dyes employed presented a severe practical drawback. By using semiconductor films consisting of nanometer-sized  $\text{TiO}_2$  particles, together with newly developed charge-transfer dyes, we have improved the efficiency and stability of the solar cell.

High-surface-area  $\text{TiO}_2$  films were deposited on a conducting glass sheet from colloidal solutions. A transmission electron micrograph of the colloid is shown in Fig. 2. Electronic contact between the particles was produced by brief sintering at 450 °C. The size of the particles and pores making up the film is controlled by the size of the particles in the colloidal solution. The internal surface area of the film is determined by the size of the particles and the thickness of the film. These parameters were optimized to obtain efficient light harvesting while maintaining a pore size large enough to allow the redox electrolyte to diffuse

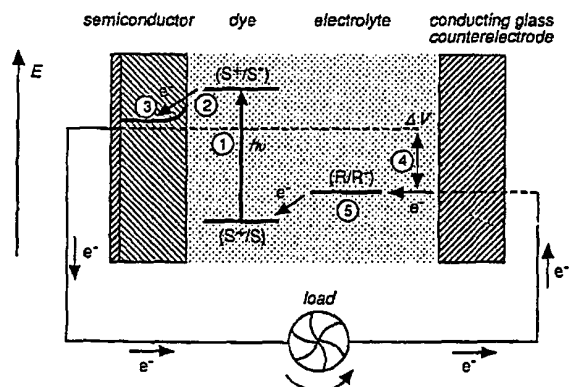


FIG. 1 Schematic representation of the principle of the dye-sensitized photovoltaic cell to indicate the electron energy level in the different phases. The cell voltage observed under illumination corresponds to the difference,  $\Delta V$ , between the quasi-Fermi level of  $\text{TiO}_2$  under illumination and the electrochemical potential of the electrolyte. The latter is equal to the Nernst potential of the redox couple ( $R/R^+$ ) used to mediate charge transfer between the electrodes. S, sensitizer;  $S^+$ , electronically excited sensitizer;  $S^+$ , oxidized sensitizer.

easily. Films of 10  $\mu\text{m}$  thickness consisting of particles with an average size of 15 nm gave linear photocurrent response up to full sunlight and were used throughout. A cubic close packing of 15-nm-sized spheres to a 10- $\mu\text{m}$ -thick layer is expected to produce a 2,000-fold increase in surface area.

Absorption spectra obtained for such nanostructured  $\text{TiO}_2$  films are shown in Fig. 3. Bare films are transparent and colourless, displaying the fundamental absorption edge of anatase (band gap 3.2 eV) in the ultraviolet region. Deposition of a monolayer of the trimeric ruthenium complex<sup>15,16</sup>,  $\text{RuL}_2(\mu\text{-(CN)Ru(CN)L})_2$ , 1, where L is 2,2'-bipyridine-4,4'-dicarboxylic acid and L' is 2,2'-bipyridine, results in deep brownish-red coloration of the film. The absorption onset is shifted to 750 nm, the light harvesting efficiency reading almost 100% in the whole visible region below 550 nm. Integration of the spectral overlap between a solar emission of AM1.5 and this absorption band shows that 46% of the incident solar energy flux is harvested by the dye coated film ( $\text{AM} = 1/\sin \alpha$  where  $\alpha$  is the angle of incidence of the solar rays at the Earth's surface).

The optical density of the film at 478 nm corrected for the absorption by the conducting glass support was 2.45. Dividing by the extinction coefficient<sup>16</sup> of 1 ( $\epsilon_{478} = 1.88 \times 10^7 \text{ cm}^2 \text{ mol}^{-1}$ ) yields the dye surface concentration,  $\Gamma = 1.3 \times 10^{-7} \text{ mol cm}^{-2}$ . As each dye molecule occupies an area<sup>16</sup> of 1  $\text{nm}^2$ , the inner surface of the film is 780  $\text{cm}^2$  for each 1  $\text{cm}^2$  of geometric surface. Thus, the roughness factor is 780, which is smaller than the predicted value of 2,000. The difference is attributed to necking between  $\text{TiO}_2$  particles. In addition, the large size of 1 prevents its access to very small pores, reducing the apparent surface area.

The photocurrent action spectrum obtained with the dye-coated  $\text{TiO}_2$  film is also shown in Fig. 3. It closely matches the absorption spectrum, indicating that the current is due to electron injection from 1 into the conduction band of  $\text{TiO}_2$ . The photocurrent yield measured at 520 nm was found to depend

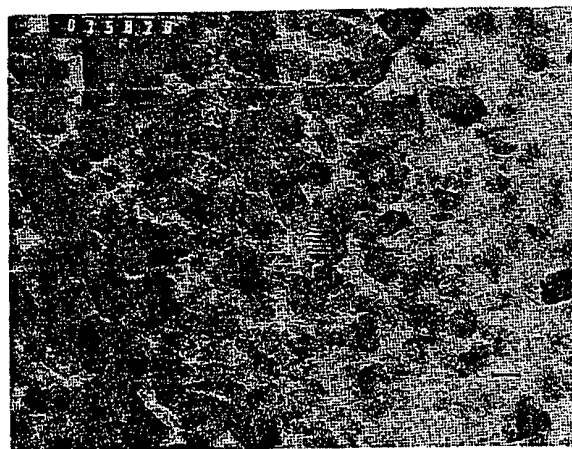


FIG. 2 Transmission electron micrograph of  $\text{TiO}_2$  particles used in thin film production. The scale bar represents 10 nm. Particles were prepared by hydrolysis of titanium tetraisopropoxide<sup>18,19</sup> followed by autoclaving for 12 h at 200 °C. To form films the sol was concentrated by evaporation of water in vacuum at 25 °C until a viscous liquid was obtained. Carbowax M-20,000 (40% by weight of  $\text{TiO}_2$ ) was added and the viscous dispersion ( $\text{TiO}_2$  content 20% by weight) was spread on the conducting glass support (Asahi glass, fluorine-doped  $\text{SnO}_2$  overlayer, transmission 85% in the visible, sheet resistance 80/square) to give a membrane of 10  $\mu\text{m}$  thickness. This was heated under air for 30 min at 450 °C. High-resolution scanning electron microscopy revealed  $\text{TiO}_2$  films to be composed of a three-dimensional network of interconnected nanoscale particles<sup>19</sup>. Transmission electron micrographs of  $\text{TiO}_2$  particles were taken before heat treatment; the annealing of 450 °C did not induce significant changes in particle size. Before dye coating, a few monolayers of  $\text{TiO}_2$  were electrodeposited onto the colloidal  $\text{TiO}_2$  film from a  $\text{Ti(III)}$  solution. Detailed description of this procedure will be published elsewhere (L. Kaven, B.O.R., A. Kay and M.G., manuscript in preparation).

on the counter ion of the iodide/triiodide redox electrolyte, increasing from 68% for tetrapropylammonium to 84% for  $\text{Li}^+$ . After correction for the light absorption by the conducting glass, the yields are 80% and 97%, respectively. This shows that the nanostructured  $\text{TiO}_2$  films used in conjunction with suitable charge transfer dyes can achieve quantitative conversion of visible light photons into electric current.

Figure 4 shows the current-voltage characteristics obtained with the thin layer cell under illumination by simulated AM1.5 solar light. The conversion efficiencies for one tenth and full sunlight are 7.9% and 7.12%, and the fill factors (maximum output power of cell ÷ [short circuit current × open circuit voltage]) are 0.76 and 0.685, respectively. Similar yields were obtained under direct sunlight (measurements performed in June early in the afternoon on the roof of the institute). Under diffuse daylight the efficiency increased to 12%, indicating that under such conditions the cell performance is better than that of conventional silicon devices. This is because the spectral distribution of diffuse daylight overlaps more favourably with the absorption spectrum of the dye-coated  $\text{TiO}_2$  film than direct sunlight. The fill factor of the cell remains above 0.7 even at very low light intensity ( $<5 \text{ W m}^{-2}$ ). Conventional photovoltaic cells have a much smaller fill factor ( $<0.5$ ) under these conditions. This indicates that loss mechanisms such as recombination, normally encountered in semiconductor photoconversion, have been minimized. This result might appear surprising in view of the disordered structure of our film giving rise to defects. But the role of the semiconductor in a dye-sensitized device is merely to conduct the injected majority charge carriers. There are no minority carriers involved in the photoconversion process. Therefore, surface and bulk recombination losses due to lattice defects, encountered in conventional photovoltaic cells, are not observed in such a device.

The long-term stability of cell performance was tested by illuminating the thin  $\text{TiO}_2$  film loaded with 1 with visible ( $\lambda > 400 \text{ nm}$ ) light for 2 months. The change in the photocurrent was less than 10% over this period, during which a charge of  $62,000 \text{ C cm}^{-2}$  was passed through the device, corresponding to a turnover number of  $5 \times 10^6$  for the sensitizer. This implies that if any dye degradation had occurred its quantum yield ( $\phi_{\text{dec}}$ ) is less than  $2 \times 10^{-8}$ . As  $\phi_{\text{dec}} = k_{\text{dec}}/\Sigma k$ , the rate constant,  $k_{\text{dec}} \text{ s}^{-1}$ , for excited-state decomposition (due to processes such as ligand loss) must be at least  $10^{-8}$  times smaller than  $\Sigma k$ , the sum of rate constants for all channels of dye deactivation. Because charge injection is the predominant channel, this sum is practi-

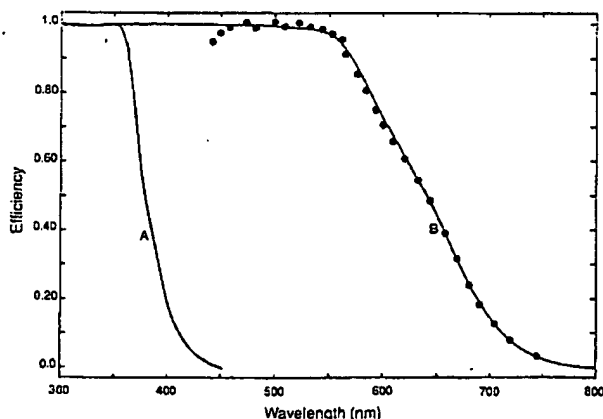


FIG. 3 Absorption and photocurrent action spectra of  $\text{TiO}_2$  films supported on conducting glass. A, absorption efficiency of the bare  $\text{TiO}_2$  film corrected for conducting glass background; B, absorption efficiency of the same film coated with a monolayer of 1; full circles, monochromatic current yield at short circuit as a function of excitation wavelength. Yield is corrected for 15% loss of incident photons through light absorption and scattering by the conducting glass support.

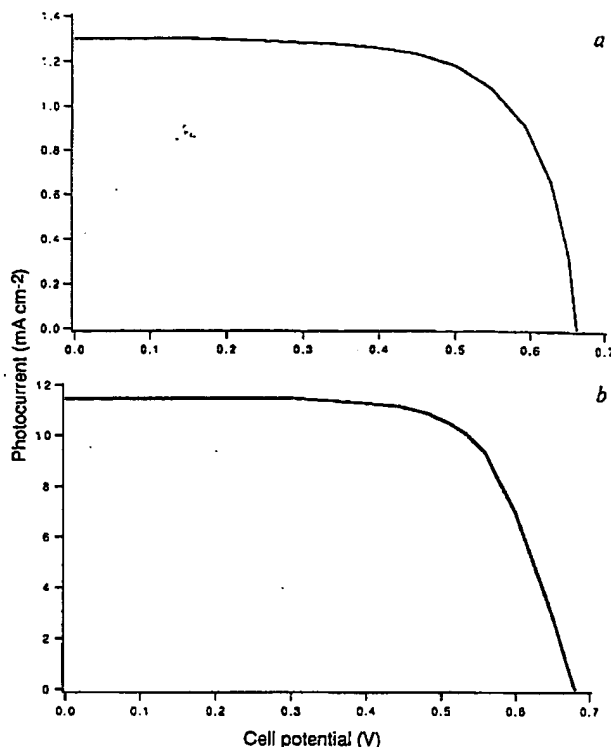


FIG. 4 Photocurrent-voltage characteristics of a cell, based on a colloidal  $\text{TiO}_2$  film sensitized by 1; the film, supported on a conducting glass sheet, was used in a sandwich-type configuration. The size of the dye coated  $\text{TiO}_2$  photoanode was  $0.5 \text{ cm}^2$ . The counterelectrode, consisting of conducting glass coated with a few monolayers of platinum, was placed directly on top of the working electrode. A thin layer of redox electrolyte is attracted into the intra-electrode space through capillary forces. The cell was exposed to simulated sunlight with AM1.5 spectral distribution. a, light intensity  $83 \text{ W m}^{-2}$ , electrolyte:  $0.5 \text{ M}$  tetrapropylammonium iodide +  $0.04 \text{ M}$  iodine in a mixture of ethylene carbonate (80% by volume) with acetonitrile. Fill factor was 0.76; surface area  $0.5 \text{ cm}^2$  (before multiplication by roughness factor). Conversion efficiency was 7.9%. b, light intensity  $750 \text{ W m}^{-2}$ , electrolyte:  $0.5 \text{ M}$  tetrapropylammonium iodide,  $0.02 \text{ M}$   $\text{KI}$  +  $0.04 \text{ M}$   $\text{I}_2$  in the same solvent. Fill factor was 0.684; conversion was 7.12%.

cally equal to the rate constant for charge injection, which exceeds  $10^{12} \text{ s}^{-1}$  in the case of 1. Therefore, the upper limit for  $k_{\text{dec}}$  is  $2 \times 10^4 \text{ s}^{-1}$ , which agrees with the known photophysics of this class of transition metal complexes<sup>17</sup>. The very fast electron injection observed with dyes such as 1, combined with high chemical stability, renders these compounds very attractive for practical development. □

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1. Bucher, K. & Frick, J. *J. Phys. Zeit* **21**, 237-244 (1980).
2. Honda, K. & Fujishima, A. *Nature* **238**, 37-39 (1972).
3. Tufts, B. J. *et al.* *Nature* **326**, 681-683 (1987).
4. Gerischer, H. *Electrochim. Acta* **35**, 1677 (1990).
5. Licht, S., Hodes, G., Tenne, R. & Mansour, J. *Nature* **326**, 863-864 (1987).
6. Heller, A. *Acc. chem. Res.* **14**, 154-162 (1981).
7. Nozik, A. J. *Phil. Trans. R. Soc. Lond.* **A295**, 453-470 (1980).
8. Tributsch, H. & Bennet, J. C. *J. electroanal. Chem.* **81**, 87 (1977).
9. Wrighton, M. S. *Acc. chem. Res.* **12**, 303-310 (1979).
10. Bard, A. J. *Science* **207**, 139 (1980).
11. Memming, R. *Phil. Tech. Rev.* **38**, 160 (1979).
12. Matsumura, M., Nomura, Y. & Tsubomura, H. *Bull. chem. Soc. Japan* **50**, 2533 (1977).
13. Alonso, N., Boley, V. M., Chartier, P. & Ern, V. *Rev. Phys. Appl.* **16**, 5 (1981).
14. Willig, F., Eichberger, R., Sundaresan, N. S. & Parkinson, B. A. *J. Am. chem. Soc.* **112**, 2702-2707 (1990).
15. Amadeti, R., Argazzi, R., Bignozzi, C. A. & Scandola, F. *J. Am. chem. Soc.* **112**, 7099-7103 (1990).
16. Nazeeruddin, M. K., Liska, P., Moser, J., Vlachopoulos, N. & Grätzel, M. *Helv. chim. Acta* **73**, 1788-1803 (1990).
17. Juris, A., Balzani, V., Barigetti, F., Campagna, S., Belzer, S. *Coord. Chem. Rev.* **84**, 85 (1988).

18. Anderson, M. A., Giese, M. J. & Xu, Q. *J. Membrane Sci.* **392**, 43 (1988).  
 19. O'Regan, B., Moser, J., Anderson, M. & Grätzl, M. *J. phys. Chem.* **94**, 8720-8726 (1990).

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## Super-spiral structures in an excitable medium

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ROTATING spiral waves have been observed in various excitable media, including heart muscle<sup>1</sup>, retinae<sup>2</sup>, cultures of the slime mould *Dicystostelium discoideum*<sup>3,4</sup> and chemical oscillators such as the Belousov-Zhabotinsky (BZ) reaction<sup>5-7</sup>. Under certain conditions the spiral wave does not exhibit simple periodic rotation, but quasiperiodic<sup>8</sup> (or 'compound'<sup>9</sup>) rotation, in which the spiral's origin (the tip) meanders<sup>10</sup>. Recent calculations<sup>11</sup> have shown that highly meandering tip motion can impose superstructures on spiral waves. Here we reproduce these patterns experimentally, using the BZ reaction as the excitable medium. We induce high tip meander by applying pulses of electrical current locally at the tip<sup>12</sup>. Image processing of the patterns reveals a spiral wave of larger wavelength superimposed on the original wave, an effect that can be described in terms of a Doppler shift in the original spiral.

All our experiments were performed in a BZ reaction<sup>13</sup> in silica gel at room temperature (20 °C). A 0.9-mm-thick gel layer containing ferroin (0.008 M) was prepared in a Petri dish. During the experiments this layer was covered with a thick (6-8 mm) solution of the other BZ reaction components: 0.1 M NaBrO<sub>3</sub>, 0.1 M CH<sub>2</sub>(COOH)<sub>2</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub>.

The highly meandering tip motion needed for the production of superstructures was enhanced by using stepwise pulses of electric current<sup>12</sup> with a period of 11 min. In each period, the voltage (1.5 V, ~5 mA) was switched on for 4 min.

The electrical circuit used (analogous to that in ref. 12) included two electrodes immersed in the liquid layer. One of these was a circular electrode which ran around the border of the Petri dish, the other was needle-shaped (0.6 mm diameter). The needle was placed over the spiral tip (3 mm into the liquid layer). Two different types of electrodes, stainless steel and platinum, were used, with the same results.

The spiral wave dynamics were followed with a video recorder connected to a PC computer. To observe super-spiral waves, simple image processing was carried out: after acquiring two successive images (separated by 2 min), we subtracted the second from the first. This same procedure was used in the calculations of ref. 11. Contrast enhancement was then used to improve the quality of the printed pictures.

Spiral waves with many turns were created by the following procedure: at the beginning of the experiment, the sulphuric acid concentration was reduced (to ~0.2 M) to avoid the spontaneous appearance of wave sources. Spiral waves were produced in this medium by the breaking of a circular wave. To increase the frequency and the number of spiral turns, sulphuric acid was added until it reached its final concentration (0.5 M). This procedure made it possible to create a single vortex of ~14 turns, with period  $T_s \approx 94$  s and wavelength  $\lambda_s \approx 0.34$  cm (Fig. 1).

After the medium had become homogeneous, the spiral waves were perturbed by switching the current on and off. This resulted in the successive increasing and diminishing of the size of the core<sup>12</sup>, so that the spiral tip described a 'flowerlet' pattern. The ratio of two frequencies associated with this motion was about six.

When this highly meandering tip motion occurs, the spiral shape becomes asymmetric. Some of the wavefronts that make up the spiral approach each other (see Fig. 2a). When the picture is processed by subtracting one image from another, a super-structure appears with the shape of a spiral wave (Fig. 2b). This super-spiral does not disappear with time, but rotates as the base spiral does; the tips of both spirals always coincide (Fig. 3). Note that the same results were observed numerically<sup>11</sup> (compare upper and lower parts of Fig. 2).

The period and wavelength of the super-spiral ( $T_{ss} \approx 540$  s and  $\lambda_{ss} \approx 2$  cm) proved to be six times as great as those of the base spiral. In contrast, the linear velocity was roughly equal for both spirals.

The super-spiral can be considered to be the result of the approach between fronts of the base spiral. In this case, the wave period detected at any point in the medium changes periodically with time. Figure 4a shows this effect, measured at a point near the centre of Fig. 2a.

The results presented in Fig. 4a can be interpreted by the Doppler effect. If we suppose that the waves of the spiral are emitted by a source rotating around a circle at constant velocity  $v_1$  and period  $T_{ss}$ , then the period of waves at any point in the medium is given by the equation

$$T(t) = T_s \left\{ 1 + \frac{v_1}{v_0} \cos \left( 2\pi \frac{t}{T_{ss}} + \phi \right) \right\} \quad (1)$$

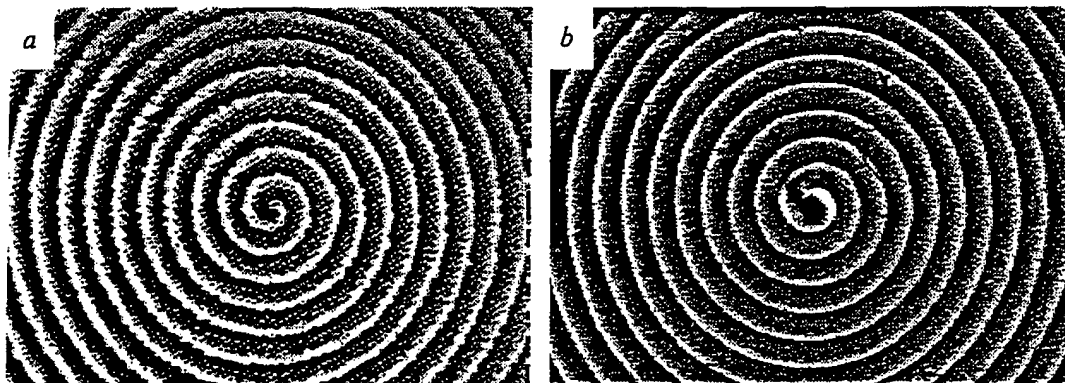


FIG. 1 Rigidly rotating spiral waves (a) for the phase-reaction/diffusion equation,  $d\phi/dt = R\{1 - \delta \sin(\phi)\} + \alpha \nabla^2 \phi + \beta |\nabla \phi|^2$  (refs 11 and 15; and P. Hanusse and V.P.M., manuscript in preparation) and (b) in the BZ reaction.

The appearance and behaviour in the two cases are strikingly similar: constant wavelength, sharp fronts and rigid rotation around the centre. The black spot in the centre of b is the electrode shadow.

Chem. Soc., 1973, 95

Manuel and L. M.

Romesberg, J. H.,  
62, 5748.

Chem. Soc., 1994, 116

Chem. Soc., 1994, 116

Chem. Soc., 1994, 116, 7949

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

J. Am. Chem. Soc.,

Fuller and D. B.

Chem. Soc., 1992, 114

J. Am. Chem. Soc.,

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

Chem. Soc., 1992, 114

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# Catechol as an efficient anchoring group for attachment of ruthenium–polypyridine photosensitisers to solar cells based on nanocrystalline TiO<sub>2</sub> films

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The Ru(II)–polypyridyl complexes [Ru(H<sub>2</sub>L)(terpy)] [PF<sub>6</sub>]<sub>2</sub> (1) and [Bu<sub>4</sub>N][Ru(H<sub>2</sub>L)(NCS)<sub>3</sub>] (2) (H<sub>2</sub>L = 4'-(3,4-dihydroxyphenyl)-2,2':6',2''-terpyridine), in which H<sub>2</sub>L is coordinated as a terpyridyl fragment with a catechol site pendant from the C4' position, adhere effectively to nanocrystalline TiO<sub>2</sub> (anatase) surfaces via the pendant catechol group; incident photon-to-current conversion efficiency values of up to 50% were obtained in their photocurrent action spectra, suggesting that the catechol unit may be a convenient and effective anchoring group for attaching dyes to TiO<sub>2</sub>-based photovoltaic cells.

Polypyridine complexes of Ru(II) are well established as photosensitisers for use on photovoltaic cells based on nanocrystalline TiO<sub>2</sub>.<sup>1</sup> There are several characteristics of the photosensitiser which need to be optimised, such as a high electron-injection efficiency from the MLCT excited state to the conduction band of the semiconductor; an absorption spectrum which matches as far as possible the solar emission spectrum; and a high affinity for the TiO<sub>2</sub> surface, which is provided by peripheral anchoring groups.

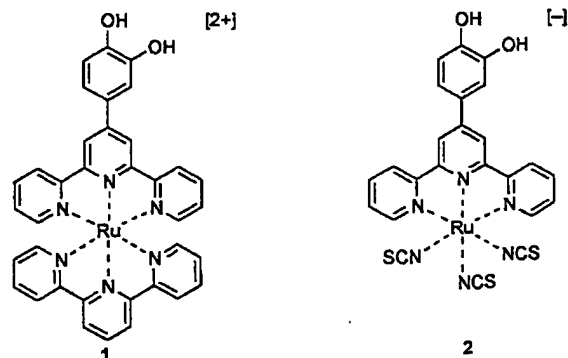
In most of the studies so far these anchoring groups are carboxylate, with the two complexes *cis*-[Ru(4,4'-dcbipy)<sub>2</sub>(NCS)<sub>2</sub>](4,4'-dcbipy = 2,2'-bipyridine-4,4'-dicarboxylic acid)<sup>2</sup> and [Ru(4,4',4''-tcterpy)(NCS)<sub>3</sub>]<sup>–</sup> (4,4',4''-tcterpy = 2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid)<sup>3</sup> being the most extensively studied; the latter of these is a particularly effective photosensitiser because its absorption spectrum extends much further into the red region of the spectrum than previous complexes. However, there are two disadvantages to the use of carboxylates as anchoring groups. Firstly their ground state pK<sub>a</sub> values are too low to ensure strong binding.<sup>4</sup> Secondly, in the presence of water, slow desorption of the photosensitisers can still occur which may limit the long-term stability of the cells. For this reason other anchoring groups have been investigated, such as the phosphonate group in the complex [Ru(Me<sub>2</sub>bipy)(HP-terpy)(NCS)] (Me<sub>2</sub>bipy = 4,4'-dimethyl-2,2'-bipyridine; H<sub>2</sub>Pterpy = 2,2':6',2''-terpyridine-4'-phosphonate) which was found to anchor to TiO<sub>2</sub> considerably more effectively than carboxylate-substituted complexes.<sup>5</sup> The difference in the binding affinity of the complexes containing carboxyl and phosphonate groups is in part due to the differences in the pK<sub>a</sub> values of the complexes. The pK<sub>a</sub> of the phosphonate group is reported as 6.5, whereas that of carboxylic acid is 3.5.<sup>6</sup>

Here we describe the investigation of ruthenium(II)–polypyridine complexes 1 and 2 (see below), containing a pendant catechol (1,2-dihydroxyphenyl) group, as photosensitisers for

photovoltaic cells. These complexes are based on the terpyridyl–catechol ligand H<sub>2</sub>L, which we first prepared a few years ago.<sup>7</sup> Since it bears a single substituent at the central C-4' position of the terpyridyl unit, it is particularly easy to prepare; and given the known affinity of catecholate for Ti(IV) ions,<sup>8</sup> and its ability to adsorb onto a TiO<sub>2</sub> surface,<sup>9</sup> these complexes seemed ideal candidates to investigate as photosensitisers.

Of the complexes, [Ru(terpy)(H<sub>2</sub>L)] [PF<sub>6</sub>]<sub>2</sub> [complex 1; H<sub>2</sub>L = 4'-(3,4-dihydroxyphenyl)-2,2':6',2''-terpyridine] was available from previous work.<sup>7</sup> [Bu<sub>4</sub>N][Ru(H<sub>2</sub>L)(NCS)<sub>3</sub>] (complex 2) was prepared by reaction of H<sub>2</sub>L with commercial hydrated RuCl<sub>3</sub> in refluxing EtOH for 3 hours, to give a precipitate of [Ru(H<sub>2</sub>L)Cl<sub>3</sub>]; reaction of this (crude) with excess potassium thiocyanate in aqueous DMF (1 : 1) at reflux for 3 hours afforded a solution containing the purple anion [Ru(H<sub>2</sub>L)(NCS)<sub>3</sub>]<sup>–</sup> which was purified by chromatography on Sephadex-G25 eluting with water, followed by precipitation as the [Bu<sub>4</sub>N]<sup>+</sup> salt. The overall yield was ca. 15%, and the complex was characterised on the basis of its negative-ion electrospray mass spectrum [*m/z* 616 (100%, {Ru(H<sub>2</sub>L)(NCS)<sub>3</sub>})<sup>–</sup> and 557 (50%, {Ru(H<sub>2</sub>L)(NCS)<sub>2</sub>})<sup>–</sup>] as well as a correct elemental analysis.

The nanocrystalline TiO<sub>2</sub> (anatase) films, of thickness 14 microns, were prepared on conducting glass using a previously described procedure.<sup>2,10</sup> The dye solutions were prepared in the concentration range of 1 × 10<sup>–5</sup> to 2 × 10<sup>–4</sup> M in ethanol. The electrodes were heated for 10 minutes at 450 °C and then allowed to reach ≈ 50 °C. The hot electrodes were dipped into the dye solution (2 × 10<sup>–4</sup> M) for 3 hours. However, when the concentration of the dye solution is 1 × 10<sup>–5</sup> M, then the dipping time was increased to 5 hours.



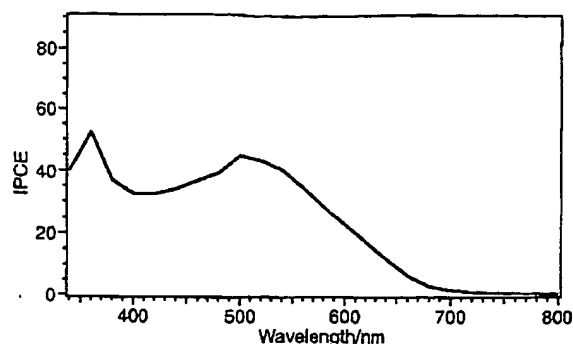


Fig. 1 Photocurrent action spectrum obtained with the complex 1 attached to nanocrystalline  $\text{TiO}_2$  films. The incident photon-to-current conversion efficiency is plotted as a function of the wavelength of the exciting light. For further details, see text.

It was noticed that the grafting properties of complexes 1 and 2, containing catechol functional groups, on to the  $\text{TiO}_2$  surface are superior and faster than those of the complexes that contain carboxylic acid groups.

The dark coloured films were tested in a photovoltaic cell† in conjunction with 600 mM dimethylpropylimidazolium iodide and 100 mM of iodine in methoxyacetonitrile as redox electrolyte. Fig. 1 shows the photocurrent action spectrum of such a cell containing complex 1, where the incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The features are similar to the absorption spectrum.<sup>7</sup> The incident photon-to-current conversion efficiency value in the peak maximum region is about 50%. The overlap integral of this curve with the standard global AM 1.5 solar emission spectrum yields a measured photocurrent density of  $5.5 \text{ mA cm}^{-2}$ ; the overall efficiency of 1 is 1.9. The open circuit potential (measured under the same irradiation intensity) is 513 mV and the fill factor is 0.67. Complex 2 under similar conditions shows a broad feature in the photocurrent action spectrum covering the entire visible spectrum up to 800 nm (Fig. 2), consistent with the known absorption properties of the  $[\text{Ru}(\text{terpy})(\text{NCS})_3]^-$  chromophore;<sup>3</sup> the IPCE value in the plateau region is about 20%. The current measured using complex 2 as sensitizer is  $3.25 \text{ mA cm}^{-2}$  and the open circuit potential is 617 mV, with a fill factor of 0.75; the overall efficiency of 2 is 1.5.

Despite the very effective anchoring of the complexes 1 and 2 onto the  $\text{TiO}_2$  surface, the measured IPCE values are lower than those obtained in related complexes using carboxylate anchor groups. A likely reason for this may be aggregation of

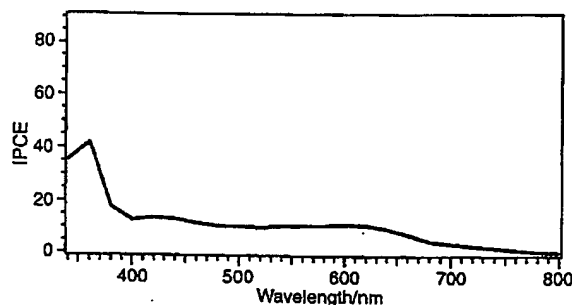


Fig. 2 Photocurrent action spectrum obtained with the complex 2 attached to nanocrystalline  $\text{TiO}_2$  films. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light. For further details, see text.

the dye molecules on the  $\text{TiO}_2$  surface. For this reason the results presented here are lower-limit and we are currently trying to improve the IPCE values by preparing the dye solutions in various solvents with different additives such as 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid (Cheno) and DMSO; we find the presence of Cheno helps to prevent surface aggregation of the sensitizer.

In conclusion it is clear that pendant catechol groups present a synthetically convenient method of anchoring photosensitizer complexes tightly to  $\text{TiO}_2$  surfaces, and are therefore of considerable promise for the development of new and more effective photosensitizers.

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## Notes and references

† The cells used for the photoelectrochemical experiments had a surface area of  $0.7 \text{ cm}^2$ , of which  $0.44 \text{ cm}^2$  was illuminated using a 450W Xenon light source focussed to give  $1000 \text{ W m}^{-2}$  (the equivalent of one sun at AM 1.5) at the surface of the test cell. The spectral output of the lamp was matched in the region of 350 to 750 nm with the aid of a Schott KG-5 sunlight filter so as to reduce the mismatch between the simulated and the true Solar spectrum to less than 2%. The differing intensities were regulated with neutral wire mesh attenuators. The applied potential and measured cell current were determined using a Keithley Model 2400 digital source meter. The counter-electrode used was platinised, fluorine-doped tin oxide glass. The current-voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process is fully automated using Wave-metrics software. A similar data acquisition system is used to control the incident photon-to-current conversion efficiency (IPCE) measurement. Under full computer control, light from a 300W Xe lamp is focussed through a high throughput monochromator onto the photovoltaic cell under test. The monochromator is incremented through the visible spectrum to generate the IPCE ( $\lambda$ ) curve as defined by:

$$\text{IPCE}(\lambda) = 1240(I_{sc}/\lambda\phi)$$

where  $\lambda$  is the wavelength,  $I_{sc}$  is the current at short circuit ( $\text{mA cm}^{-2}$ ) and  $\phi$  is the incident radiative flux ( $\text{W m}^{-2}$ ). This curve can be derived from the measured absorption spectrum of the adsorbed photosensitizer for comparison.

- 1 M. Grätzel, *Prog. Photovoltaics*, 2000, 8, 171.
- 2 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, 115, 6382.
- 3 M. K. Nazeeruddin, P. Péchy and M. Grätzel, *Chem. Commun.*, 1997, 1705.
- 4 M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C. H. Fischer and M. Grätzel, *Inorg. Chem.*, 1999, 38, 6298.
- 5 S. M. Zakeeruddin, M. K. Nazeeruddin, P. Péchy, F. P. Rotzinger, R. Humphry-Baker, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1997, 36, 5937.
- 6 M. Montalti, S. Wadhwa, W. Y. Kim, R. A. Kipp and R. H. Schmehl, *Inorg. Chem.*, 2000, 39, 76.
- 7 B. Whittle, N. S. Everest, C. Howard and M. D. Ward, *Inorg. Chem.*, 1995, 33, 2025.
- 8 B. A. Borgias, S. R. Cooper, Y. B. Koh and K. N. Raymond, *Inorg. Chem.*, 1984, 23, 1009.
- 9 (a) R. Rodriguez, M. A. Blesa and A. E. Regazzoni, *J. Colloid Interface Sci.*, 1996, 177, 122; (b) Y. Liu, J. I. Dadap, D. Zimdars and K. B. Eisenthal, *J. Phys. Chem. B*, 1999, 103, 2480; (c) P. A. Connor, K. D. Dobson and A. J. McQuillan, *Langmuir*, 1995, 11, 4193; (d) G. Redmond, D. Fitzmaurice and M. Grätzel, *J. Phys. Chem.*, 1993, 97, 6951.
- 10 C. J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover and M. Grätzel, *J. Am. Ceram. Soc.*, 1997, 80, 3157.

## Microwave thermal gra interface

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Microwave activa the electrode|sol cavity. Considera reduction of  $\text{Ru}(\text{N}^{\text{O}})$  dication ( $\text{MV}^{2+}$ ):  $\text{MV}_{\text{an}}^{\text{O}}$  and  $\text{MV}_{\text{crp}}^{\text{O}}$  with conventiona the electrode, (ii) t magnitude higher temperature.

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## 1 Introduction

Microwave activa ly been shown t temperature conc electrode|solutio systems. The dis tool in chemistry synthesis,<sup>7</sup> has tri wave radiation e may offer a new : at interfaces in t By coupling mic the chemical pro processes, benei methods of empl or better contr example, photo-radio-frequency tion. In particul workers<sup>14-18</sup> ha activation in elec Self-focussing in front of a wor shown to have process, to affect and to occur or perturbation at microwaves on : nucleation of co electrode|solutio ccesses have yet t of microwaves a